Effects of ultrasound on the electrodeposition of lead dioxide on glassy carbon electrodes

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The electrodeposition of lead dioxide from lead(II) nitrate in an acid medium has been used as a test reaction to study the effects of an ultrasound field. The different behaviours found between platinum and glassy carbon electrodes have been compared by means of cyclic voltammetry and simple potential steps. The current–time response for a platinum electrode is not affected by the presence or absence of ultrasound; in contrast, significant changes have been observed in the characteristic regions of these curves (induction time $t_i$) with the glassy carbon electrode. Scanning electron microscopy (SEM) has been employed to follow changes in the surface topography after the electrodes had been exposed to ultrasound. Results indicate that neither pits nor structural modifications that may increase the electrode surface occur with the device used. It is concluded that the activation of glassy carbon electrodes by the action of an ultrasound field for electrodeposition of lead dioxide is associated with the surface functionalization caused by the reaction of OH$^-$ radicals (derived from aqueous sonolysis) with the carbon surface.

Nowadays, the influence of ultrasound on the electrochemical behaviour of different systems is a very active field of research. Thus, beneficial effects have been found on mass transport, on activation of the electrode surface, on adsorption processes, and on the modifications that occur in the reaction mechanisms due to radical generation when electrochemical processes are carried out under ultrasonic irradiation. In most of these studies the reduction of ferrocyanide anion, methylviologen, $p$-benzoquinone, copper sulfate, and the oxidation of pyrrole have been used as test reactions in order to obtain information on the changes that occur in the different types of electrochemical processes. The influence of ultrasounds on the electrode surface of different materials have also been studied. Coury and coworkers have studied substrates such as glassy carbon, Ebonex, Pt, Au, W and Pd, and they have laid great stress on the effects of ultrasound on glassy carbon.

A wide diversity of methods have been reported for the treatment and activation of surfaces of carbon electrodes. There are very different and even controversial opinions about the reproducibility of the results. In any case, there is agreement that the oxidation of the surface of glassy carbon provides an increase in the activity of the electrode. In this context, we can also find in the literature other studies in which pretreatment with ultrasound of the electrode surface provides an increase in the activity of the electrode.

In this paper we propose the electrodeposition of lead dioxide from soluble salts of Pb$^{II}$ as a test reaction to study the effects of ultrasound on the electrode surface. Fleischmann et al. were the first to investigate the mechanism for the electrodeposition of lead dioxide. They suggested the following mechanism:

\[ \text{OH}^- \leftrightarrow \text{OH}_{\text{ads}} + e^- \]  
\[ \text{Pb}^{2+} + \text{OH}_{\text{ads}} + \text{OH}^- \rightarrow \text{Pb(OH)}_{2,\text{ads}}^+ \text{(slow)} \]  
\[ \text{Pb}^{2+} + \text{OH}_{\text{ads}} + \text{OH}^- \rightarrow \text{Pb(OH)}_{2,\text{ads}}^{2+} + e^- \text{(slow)} \]  
\[ \text{Pb(OH)}_{2,\text{ads}}^{2+} \leftrightarrow \text{PbO}_2(s) + 2\text{H}^+ \]

Several authors, like Chang and Johnson and Velichenko et al., have recently proposed some modifications to this mechanism. Thus, they suggest that the mechanism involves the generation of some soluble intermediates, which can be withdrawn from the electrode surface by means of convective–diffusional processes. Anyhow, it should be noted that the first step in the mechanism (generation of OH$_{\text{ads}}$) has been widely accepted.

Experimental

All experiments were carried out using a VoltaLab electrochemical system consisting of a DEA 352 potentiostat and an IMT 102 electrochemical interface. The system was connected to a personal computer for recording and treatment of curves. Electrochemical experiments were performed in a typical all-glass two-compartment voltammetric cell (50 mL volume) placed just over the transducer of a Selecta commercial ultrasonic bath (30 kHz, 100 W). The cell was immersed in such a way that the level of both liquids (bath and electrolyte) was the same. The level of the bath liquid was 6 cm from the bottom, and this was the separation distance between the transducer and the electrode surface (Fig. 1). The system was thermostatted by recirculating water at a constant temperature of 25 $^\circ$C.

The working electrodes were a polyoriented platinum electrode and a glassy carbon rod. A platinum wire acted as the counter electrode. Platinum electrodes were cleaned by...
heating to red heat and quenching in water prior to each experiment. Before each experiment, glassy carbon electrodes were polished, first with fine emery paper, then with decreasing size alumina particles in suspension on a polishing cloth, until a mirror finish was obtained. In both cases, electrodes were thoroughly rinsed with water. A SCE served as the reference electrode.

The chemicals were Analar quality. Aqueous solutions of 0.1 M lead(II) nitrate–1 M nitric acid were prepared using ultrapure water obtained from a Millipore Milli-Q system. Solutions were thoroughly purged of oxygen prior to sweeping by bubbling with nitrogen N50 (Air Liquide) for 20 min. Nitrogen N50 (Air Liquide) was also used for saturation gassing of the solutions before each experiment. During measurements a flow of gas was passed over the solution surface.

A JSM-840 JEOL scanning electron microscope was employed to obtain topographical views of the electrode surfaces.

Results

Voltammetry

Fig. 2 shows the cyclic voltammogram of the electrodeposition of lead dioxide from 0.1 M Pb(NO₃)₂ + 1 M HNO₃ on a platinum electrode recorded under silent (a) and ultrasonic (b) conditions. Fig. 3 shows the same experiment on a glassy carbon electrode. The voltammetric response for platinum is the same under both silent and ultrasonic conditions, except in the mass transport control region, as might be expected. Analogous behaviour is observed for a glassy carbon electrode. However, the potential at which electrodeposition begins is different for each electrode. It can, therefore, be deduced that the activation overpotential for platinum is significantly less that that for glassy carbon. This same behaviour, which has also been observed for the oxygen evolution process, is consistent with the conclusion drawn by many researchers, whereby the initial step (eqn. 1) in the lead dioxide electrodeposition mechanism is the same as that for
oxygen evolution on a variety of electrodes. It is noteworthy
that the electric charge of the stripping process of lead dioxide
on platinum ($E \approx 1130$ mV vs. SCE) is less than the electric
charge on glassy carbon. This is a consequence of the poor
adherence of lead dioxide to the platinum electrode, as is
demostrated by the presence of lead dioxide flakes at the
bottom of the cell during the experiment.

**Chronoamperometry**

Potential step experiments were performed in two stages. In
the first stage, the electrode was held in an open circuit ($i = 0$
for $30$ s. In a second stage, and immediately after, a potential
step that has been fixed beforehand was carried out. In some
experiments (Fig. 6), the electrode underwent additional
pretreatment with ultrasound in which the variable was the
duration of this pretreatment.

Fig. 4 shows the $j-t$ profiles for lead dioxide deposition on a
polyoriented platinum electrode under silent (a) and ultrasonic
conditions (b) for two steps of different amplitudes. It can be
seen that both transient curves are very similar but with
slightly lower $j$ values in the presence of ultrasound.

Fig. 5 shows the chronoamperomteric transients for a glassy
carbon electrode under silent (a) and ultrasonic conditions (b)
for two steps of different amplitudes. In this case, a strong
influence of the ultrasound field can be pointed out. Thus,
the induction time under ultrasonic conditions is less than under
silent conditions and the current density is higher under ultra-
son than under silent conditions. Coury and coworkers have
shown that glassy carbon and Ebonex electrodes are
severely pitted under ultrasound in aqueous media. This is
one of the reasons they argue against the use of glassy carbon
for sonochemical studies in aqueous media. Scanning
electron microscopy (SEM) has been employed to follow
changes in the surface topography before and after the elec-
rodes had been exposed to ultrasound in electrolytic medium
for $20$ min. No damage of the surface was observed. A very
pausible explanation of this different behaviour is the experi-
mental approach used in both experiments. Thus, Coury and
coworkers used a sonochemical reactor that allows a
sonic horn to be located a very short distance away from the
electrode surface. In our work, we immersed the electrochemi-
ical cell in the ultrasonic bath, and it is known that in this
configuration the ultrasound power transmitted is much lower
than in the other arrangement.

Fig. 6 shows the superposition of $j-t$ profiles recorded in a
quiescent solution on a glassy carbon electrode (pretreated in situ with ultrasound for different times) and in solution under
ultrasound. On increasing the pretreatment times, the $j-t$
curve recorded under quiescent conditions becomes similar to
the response recorded under ultrasound.

Fig. 7 shows the superposition of potential-time curves
prior to the chronamperometric experiment for the $20$ min
pretreatment curve and the curve recorded under ultrasound
shown in Fig. 6. The electrode potential for surfaces pre-
treated with ultrasound is always held constant within a short
interval.

Fig. 8 shows the scanning electron micrographs (SEMs) cor-
responding to a graphite surface before and after sonication
($20$ min) in the same electrolytic medium. No appreciable
surface effect is evident.

Fig. 9 shows the SEMs of the lead dioxide electrodeposition
process at the induction period ($400$ s) under quiescent condi-
tions and under ultrasound. It is evident that the influence of
ultrasound increases considerably the number of particles of
lead dioxide deposited at the same potential.
Discussion

The interpretation of the cyclic voltammetry curves provides little information about the effects of an ultrasonic field on the electrodeposition process. However, other electroanalytical techniques like chronoaamperometry have been useful to contribute details of the process.

Chronoaamperometric experiments have shown that the results obtained for platinum and glassy carbon are different. No noticeable effect is produced on platinum electrodes. The small decrease in the current density has also been observed by other workers\textsuperscript{26,27} under convective conditions. In contrast, the response for the glassy carbon electrode shows a more complex reaction. This makes the existence of effects located on the electrode surface evident. SEMs confirm that the surface of the sonicated electrode does not exhibit any signs of superficial pitting or damage. Therefore, no modifications of the geometric area must be expected for electrochemical measurements.

On the other hand, some new signs have been found regarding the formation of functional groups on the surface of the electrode during sonication. These functional groups persist with time. This phenomenon had previously been observed by Coury and coworkers using other test reactions and techniques.\textsuperscript{13,19} When lead dioxide electrodeposition is used as a test reaction, these functional groups play a very active role in the electrodeposition mechanism (reaction 1) as an intermediate product, and they can be consumed within the process of lead dioxide deposition. This is evident in the decreasing induction time as the pretreatment time increases (or by recording the curve under ultrasound). In addition, the idea of the functionalization of the glassy carbon electrode surface as a consequence of action of ultrasound on the surface is reinforced by the different behaviour in the $E-t$ response for pretreated and non-pretreated electrodes. The fact that the potential remains constant with time for pretreated electrodes is evidence that treatment provides a stable surface, in contrast with non-pretreated electrodes, whose surfaces undergo changes with time, as the spontaneous variation of the potential at open-circuit indicates. The reaction of the hydroxyl radical OH$^-$ derived from aqueous sonolysis, with the free carbon surface catalyses the nucleation process on the surface, decreasing the induction time for a constant step potential. This decrease depends on pretreatment time.

Conclusion

The results described in this paper show that the application of an ultrasound field activates the lead dioxide electrodeposition on glassy carbon surfaces. The enhancement of this process is probably associated with an increase in the density of electroactive superficial oxides. Thus, glassy carbon is a suitable material for the kinetics studies of these processes and for other studies in which eqn. 1 occurs.

The design of the experiment used in this work can be appropriate for mechanistic studies in sonoelectrochemistry with non-metals, which are severely damaged by sonic horns located a short distance away from the electrodes.

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